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We have focused our efforts on the development of novel electrochemical cells for improved EXAFS spectroelectrochemistry and the characterization of a number of chemical systems for EXAFS analysis. These systems include: $\text{Fe}(\text{bipy})_3(\text{ClO}_4)_2$, $\text{Ru}(\text{bipy})_3\text{Cl}_2$, and $\text{Cu}(\text{dmp})_2\text{BF}_4$ (bipy = 2,2'-bipyridine, dmp = 2,9-dimethyl-1,10-phenanthroline) in solution at reticulated vitreous carbon electrodes, and incorporated in Nafion films on gold Mylar and colloidal graphite gold Mylar electrodes; $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{Co}(\text{phen})_3\text{Cl}_3$, $\text{Fe}(\text{bipy})_3\text{ClO}_4$ and $\text{K}[\text{Cu}(\text{bcp-s})_2]$ (phen = 1,10-phenanthroline, bcp-s = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline-disulfonic acid) incorporated in the solid polyelectrolytes poly(dimethyldiallylammonium chloride) and poly(acrylamide) on gold minigrid electrode in a humidistatic cell; and Prussian Blue, $\text{KFe}(\text{Fe}(\text{CN})_6)$, cyanometalate films electrochemically deposited onto gold Mylar electrodes. The above chemical systems display both good electrochemical and chemical reversibility essential for the electrochemical experiment.

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January 27, 1989

Dr. John S. Wilkes
Program Manager
Directorate of Chemical and Atmospheric Sciences
Department of the Air Force
Air Force Office of Scientific Research
Bolling Air Force Base, DC 20332-6448

Re: Interim report for grant #AFOSR-88-0089 entitled, "X-ray Absorption Spectroscopy of Electrochemically generated Species". Principal investigators: Richard C. Elder and William R. Heineman at the University of Cincinnati

Dear Dr. Wilkes:

Our research in EXAFS spectroelectrochemistry can be divided into three areas; development of modified electrodes, design of new electrochemical cells, and characterization of specific chemical systems. Each of these aspects of the project is considered individually below.

Earlier studies utilized electrodes constructed from gold minigrid, colloidal graphite, and reticulated vitreous carbon (RVC). The use of gold minigrid electrodes has been demonstrated for spectroelectrochemical studies and is utilized in the present study concerning solid state polyelectrolyte cells. Graphite film electrodes, prepared by spraying colloidal graphite onto a Mylar® substrate, are more transparent to X-rays, however, the IR drop across the electrode surface retards electrochemical conversion. RVC electrodes display very facile electrode kinetics and have been utilized successfully in solution EXAFS cells. In the past year we have investigated the use of thin (300Å) gold film electrodes produced by evaporating gold onto a Mylar® substrate. This electrode functions electrochemically as well as a gold disk electrode. The advantage of this electrode is that it is transparent in the visible region of the spectrum allowing for optical spectroelectrochemical characterization of the electrode modified with a polymer film. This is an important characterization procedure with which we can ensure that the polymer-redox system is functioning properly for the EXAFS spectroelectrochemical experiment. These experiments have been performed on $\text{Fe}(\text{bipy})_3(\text{ClO}_4)_2$, $\text{Ru}(\text{bipy})_3\text{Cl}_2$, and $\text{Cu}(\text{dmp})_2\text{BF}_4$ incorporated in a Nafion® film (bipy = 2,2'-bipyridine, dmp = 2,9-dimethyl-1,10-phenanthroline). In order to obtain a good EXAFS signal, one needs a large amount of metal complex (on the order of a milligram) in the X-ray beam. We have found that a polymer film which is thick enough to accommodate this amount of material is generally too thick for complete electrochemical conversion at the gold/mylar® electrode in a reasonable time. To alleviate this problem, a "layered sandwich" electrode was utilized. This electrode was constructed by coating the gold/Mylar® electrode with alternating layers of colloidal graphite and Nafion® solution in which the metal complex was dissolved. The Nafion® solution soaks into the graphite layers resulting in

a relatively homogeneous structure. The graphite provides a mechanism for charge transport through the relatively thick Nafion[®] film. We have performed XANES spectroelectrochemistry on Cu(dmp)₂BF₄ in this electrode and have demonstrated the utility of the electrode and the chemical reversibility of this system.

A new solution cell utilizing a RVC working electrode, a Pt foil counter electrode, and two Ag/AgCl reference electrodes has recently been constructed. This cell offers three advantages over earlier designs. The main advantage is that the RVC electrode fits tightly against both windows of the cell. This design offers better electrochemical conversion of the solution in the X-ray beam compared to the old design which had a "dead volume" between the windows and the working electrode. Secondly, the increased surface area of the Pt foil counter electrode allows for more rapid electrochemical conversion. Finally, the cell is constructed out of Macor[®], a ceramic material, in anticipation of performing nonaqueous work in the future. This cell has been tested using Cu(dmp)₂BF₄ for both XANES and visible spectroelectrochemical experiments. Very good electrochemical conversion of this copper complex was observed.

A new area of investigation involves the electrochemical deposition of cyanometalate films such as Prussian Blue, KFe[Fe(CN)₆]. Thick Prussian Blue films can be deposited onto gold/Mylar[®] electrodes by applying a 0.5 V vs. SCE potential to the gold electrode in an aqueous, acidic solution of FeCl₃ and K₃Fe(CN)₆. When placed in fresh electrolyte, this film displays reversible electrochemistry, and complete reduction of a film thick enough for the EXAFS experiment is easily accomplished.

Over the past year we have placed considerable effort in studying solid-state electrochemistry utilizing water soluble ion exchange polymers. We have targeted two such polymers in this study; poly(dimethyldiallylammonium chloride), p-DMDAAC; and poly(acrylamide), p-AA. In order for the p-DMDAAC and p-AA to be sufficiently conductive for the electrochemical experiment, they must be kept moist. To accomplish this, we have developed an electrochemical cell which maintains a constant humidity of 92%. In this humid environment, the polymers absorb sufficient moisture to be conductive, however, not so much that they start to "flow" across the electrode out of the X-ray beam. Several metal complexes have been incorporated into these polymer films and completely converted electrochemically to their different oxidation states. Complexes include; K₃Fe(CN)₆, Co(phen)₃Cl₃, Fe(bipy)₃(ClO₄)₂, and K₃Cu(bcp-s)₂ (phen = 1,10-phenanthroline, bcp-s = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline-disulfonic acid). It is interesting to note that both anionic and cationic complexes partition into both polymers despite the cationic functional groups of the p-DMDAAC and the anionic functional groups in p-AA (pH=9). We have also been investigating the effect of cross linking the polymers using γ -irradiation.

A highly conductive polymer (conductivity up to 40 S/cm) can be synthesized by the copper induced polymerization of 3-methylthiophene. The resulting polymer has been found to contain 30% by weight copper as measured by atomic absorption analysis. We have been interested in determining the coordination environment around the copper centers in this polymer using EXAFS. The polymer was presumed to be cross-linked by copper coordination to the sulfur atoms of the thiophene rings. This would provide a four coordinate copper-sulfur environment. Analysis and curve fitting of the filtered EXAFS data indicates that copper is not coordinated to sulfur but rather it is most likely coordinated to oxygen. Water present in the polymer matrix is probably the source of the oxygen.

This year we have obtained only two days of useful X-ray beam time at the National Synchrotron Light Source (NSLS), and no time at the Stanford Synchrotron Radiation

Laboratory (SSRL) due to the commissioning of the Stanford Linear Collider (SLC) and the budget reductions given SSRL by DOE. Consequently, we have used this year primarily to develop new electrochemical cells and study various polymer-redox systems. We now have a number of well-understood systems "in-line" for the EXAFS measurements. 1989 is looking promising. We are scheduled at NSLS for a 24 hour run on February 4 and a seven day run at SSRL from March 2-8. We also expect more time at both SSRL during their next dedicated run in June or July and at NSLS later this year. This represents a huge increase in beam time, however, we will be able to use it effectively as a result of the number of chemical systems developed over the past year.

Our plans for 1989 involve the EXAFS study of the above mentioned systems. We also plan to explore some new polymer-redox systems synthesized using polymers containing functional groups that can coordinate metal centers. These structures can be produced by reacting a metal complex with the polymer film. For example, the coordination of an iron center to a polypyridine film. A second method would involve the electropolymerization of a complex containing polymerizable functional groups. An good example of this would involve the complex $\text{Ru}(\text{bipy})_2(4\text{-vpy})_2(\text{BF}_4)_2$ (4-vpy= 4 vinylpyridine). This complex can be electropolymerized by cycling an electrode between -1.5 and -2.0 V vs. a quasi silver reference electrode which results in the growth of the polymer film on the electrode..

We anticipate the addition of a new postdoctoral fellow, Eric Kristensen, on the first of February. This is in addition to Lee R. Sharpe (postdoctoral fellow) and David H. Igo (graduate student) presently involved with the project. Lee Sharpe has accepted a position at Grinnell College and will be leaving the project in July. Another postdoctoral fellow who is not supported by this grant, Jon Kirchhoff, has synthesized some of the compounds under investigation. We have purchased a Bioanalytical Systems BAS-100 Electrochemical Analyzer and an ultrasonic cleaner. The BAS-100 was chosen instead of the BAS CV-27 and X,Y recorder originally written into this grant because of its greater versatility and, being a demo unit, it was available at half price. The cost was only slightly more than the combined price of the CV-27 and X,Y recorder. The BAS-100 has been interfaced to a IBM XT compatible computer allowing for the storage of data and background subtraction. The ultrasonic cleaner is used to clean various electrodes prior to the electrochemical experiments.

Sincerely,



Richard C. Elder
Professor of Chemistry



William R. Heineman
Distinguished Research Professor

ABSTRACT

Re: Interim report for grant #AFOSR-88-0089 entitled, "X-ray Absorption Spectroscopy of Electrochemically generated Species". Principal investigators: Richard C. Elder and William R. Heineman at the University of Cincinnati

Our research concerns the study of the change in the coordination environment and bond length about transition metals in complexes incorporated in a variety of media using EXAFS spectroelectrochemistry. Over the past year we have obtained only two useful days of synchrotron X-ray beam time. Consequently, we have focused our efforts on the development of novel electrochemical cells for improved EXAFS spectroelectrochemistry and the characterization of a number of chemical systems for EXAFS analysis. These systems include: $\text{Fe}(\text{bipy})_3(\text{ClO}_4)_2$, $\text{Ru}(\text{bipy})_3\text{Cl}_2$, and $\text{Cu}(\text{dmp})_2\text{BF}_4$ (bipy= 2,2'-bipyridine, dmp= 2,9-dimethyl-1,10-phenanthroline) in solution at reticulated vitreous carbon electrodes, and incorporated in Nafion[®] films on gold Mylar[®] and colloidal graphite gold Mylar[®] electrodes; $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{Co}(\text{phen})_3\text{Cl}_3$, $\text{Fe}(\text{bipy})_3(\text{ClO}_4)_2$, and $\text{K}_3\text{Cu}(\text{bcp-s})_2$ (phen= 1,10-phenanthroline, bcp-s= 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline-disulfonic acid) incorporated in the solid polyelectrolytes poly(dimethyldiallylammonium chloride) and poly(acrylamide) on gold minigrid electrode in a humidistatic cell; and Prussian Blue, $\text{KFe}[\text{Fe}(\text{CN})_6]$, cyanometalate films electrochemically deposited onto gold Mylar[®] electrodes. The above chemical systems display both good electrochemical and chemical reversibility essential for the electrochemical experiment. Our plans for 1989 involve the EXAFS study of the above mentioned systems and new polymer systems having functional groups capable of coordinating metal centers. We have already been assigned eight days of X-ray beam time with the expectation of more time during the next dedicated run at SSRL in June or July. This will enable us to catch up on the EXAFS experiments.